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APPLICATION OF NUCLEAR IRRADIATION TECHNIQUES TO THE TAILORING OF SEMICONDUCTOR PROPERTIES

by

John E. Fischer

Research Department



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ABSTRACT. Nuclear irradiation has a profound influence on the electrical, optical and physical properties of semiconductors. These effects are usually viewed as "radiation damage", degradation in a nuclear environment leading ultimately to device failure. Recently, several irradiation techniques have been employed to produce beneficial changes in bulk semiconductor materials, leading either to improved device performance or to otherwise impossible device structures. We briefly review several of these techniques, with emphasis on opto-electronic devices. We also review the basic research literature which led to the proposal of a new optimization possibility; its feasibility is being studied under the IED project "Extended Long Wavelength Cutoff for Silicon Surface Barrier Detectors".

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FOREWORD

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13. ABSTRACT

Nuclear irradiation has a profound influence on the electrical, optical and physical properties of semiconductors. These effects are usually viewed as "radiation damage", degradation in a nuclear environment leading ultimately to device failure. Recently, several irradiation techniques have been employed to produce beneficial changes in bulk semiconductor materials, leading either to improved device performance or to otherwise impossible device structures. We briefly review several of these techniques, with emphasis on opto-electronic devices. We also review the basic research literature which led to the proposal of a new optimization possibility; its feasibility is being studied under the IED project "Extended Long Wavelength Cutoff for Silicon Surface Barrier Detectors".

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THE RADIATION DAMAGE PROCESS

There are two basic classes of nuclear irradiations: those which affect the material simply by knocking an atom off its normal lattice site, and those which actually introduce new chemical species into the target sample (Ref. 1). In the former category are electrons from ~ 100 KeV to hundreds of MeV, gamma rays which produce energetic electrons "internally" via pair production and photoelectric effects (~ 100 KeV threshold), protons from a few KeV to many GeV, neutrons from a few KeV on up, and other charged particles (deuterons, alpha particles, etc.). The latter category will be ignored for the remainder of this report; ion implantation and thermal neutron transmutation are two processes of this type.

All semiconductor properties are affected by irradiation, to a greater or lesser extent. Grossly speaking, the "sensitivity scale" of semiconductor parameters is (starting with the most sensitive):

1. Minority carrier transport properties (diffusion length, lifetime).
2. Majority carrier transport properties (carrier concentration, mobility).
3. Optical properties involving discrete energies (new IR absorption bands appear, the fundamental edge shape changes).
4. Physical properties and integral optical properties (lattice constant, thermal conductivity, index of refraction).
5. The ultimate stage is in dispute--some people feel that eventually one arrives at a totally disordered state, equivalent to that obtained by vacuum deposition on a cold substrate.

It is well known that different specific defects influence different properties (Ref. 2), at least in the early stages of irradiation when one can still think in terms of discrete defect levels in the forbidden gap. It is also known that the "inventory" of defects after irradiation depends critically on the impurities present in the target material (Ref. 3), as well as the specific irradiation conditions employed. This results from the fact that the products of a primary collision event, vacancy plus interstitial, are extremely mobile except at cryogenic temperatures, and that stable defects consist of agglomerations of

vacancies and interstitials with impurities (and with each other). Thus the "final state" of an irradiated specimen depends on:

1. Initial impurities
2. Type and energy of irradiating projectile
3. Amount of irradiation
4. Temperature of irradiation

The opto-electronic behavior of semiconductors is governed by majority and minority carrier transport and optical absorption, so irradiation effects on devices of this type are very difficult to predict. The most extensively studied system is the response of silicon solar cells to proton irradiation (Ref. 4); cell efficiency is drastically reduced by degradation of minority carrier diffusion length, caused by protons trapped in the Van Allen belts.

In the remainder of this report we discuss four instances in which nuclear irradiation is beneficial to the operation or construction of a semiconductor detector. These are:

1. Gamma ray compensation of germanium, for totally depleted x-ray spectrometers.
2. Conversion of p-type InSb to n-type by proton irradiation, for n-on-p junction photodetectors.
3. Introduction of new IR absorption bands in silicon by 10 MeV electrons, for selective IR detection at ~ 2 and ~ 4 microns.
4. Alteration of the shape of the fundamental absorption edge of silicon, using neutrons or 50 MeV electrons, for extended cutoff Schottky barrier detectors and/or fast 1.06μ detectors.

The first three concepts have been demonstrated on a laboratory scale. The fourth is the subject of an IED study in Code 6019; in this report we review the basic research results which suggest the feasibility of such a detector.

GAMMA RAY COMPENSATION

Assume an x-ray photon of energy E traversing a semiconductor of band gap E_g ; the semiconductor is thick enough to stop the photon. A number of electron-hole pairs equal to $E/2 E_g$ is produced along the x-ray's path; if all these carriers can be detected at suitable electrodes, the height of the current pulse is proportional to the x-ray energy. To achieve this, the semiconductor must be "totally depleted"; that is, a large electric field must be present throughout the bulk of the detector, so that the photocarriers will drift rapidly to the

electrodes before recombining. Total depletion can be achieved with a back-biased Schottky barrier if the bulk material is intrinsic. These detectors are usually operated at liquid nitrogen temperature to reduce noise. The intrinsic carrier concentration at 77°K is many decades below the density of residual ionized impurities, so it is necessary to compensate the residual donors with a dopant which introduces a deep acceptor level into the forbidden gap. This acceptor must be lower in energy than the Fermi level at 77°K in order that the excess electrons from the residual donor impurities be frozen out.

To date, the best compensated x-ray spectrometers have been obtained with lithium-drifted Ge and Si; lithium introduces the required deep acceptor, and low-noise, totally depleted Schottky diodes result. Unfortunately, the rapid diffusion of lithium requires that the detector be maintained at 77°K, otherwise compensation near the junction is lost. The detector is effectively ruined if allowed to warm up to room temperature.

This problem can be alleviated by using a radiation-induced defect as a compensating acceptor (Ref. 5). Irradiation with gamma rays emitted by cobalt-60 produces such a defect, with a compensating level 0.2 eV below the conduction band (Ref. 1). The defect responsible is probably a lattice vacancy trapped by a substitutional antimony atom. Such an irradiation does not introduce any gross damage, since the photoelectrons produced by cobalt-60 gamma rays have a maximum energy of 1.33 MeV. The maximum energy transferred to a lattice atom by a 1.33 MeV electron is only a few times the lattice binding energy, so the displaced atom has enough kinetic energy to displace at most three or four other lattice atoms.

The success of this method rests largely on the quality of the starting material. Large dislocation density is to be avoided for two reasons (Ref. 5). Some of the radiation-induced vacancies and interstitials can be trapped by dislocations, where they do not produce compensating levels; a longer irradiation is therefore needed to achieve a given level of compensation if dislocations are present. Furthermore, the defects associated with dislocations apparently degrade the response time of the detector, by introducing shallow trapping levels into the forbidden gap. The recovery time after an x-ray pulse at 77°K can be unusually long in this case.

We have had some experience with gamma-ray-compensated Ge in connection with the electroreflectance program (Ref. 6). Starting ingots were not chosen with any special care. Irradiations were performed by Oak Ridge National Laboratory. Some samples were hardly compensated at all after 10^{18} gammas/cm², while others had 80°K resistivity of 4×10^7 ohm-cm (residual ionized donor density $10^7 - 10^8/\text{cm}^3$).

Two additional possible applications for gamma-compensated Ge are:

1. Thermometry--a six decade resistance change over a 220°K temperature range should be useful in some applications.
2. Sensitive near IR detectors--if trapping can be avoided, intrinsic Ge at 77°K should be an excellent detector from 0.9 - 1.8 microns.

n-ON-p InSb PHOTODIODES BY PROTON BOMBARDMENT

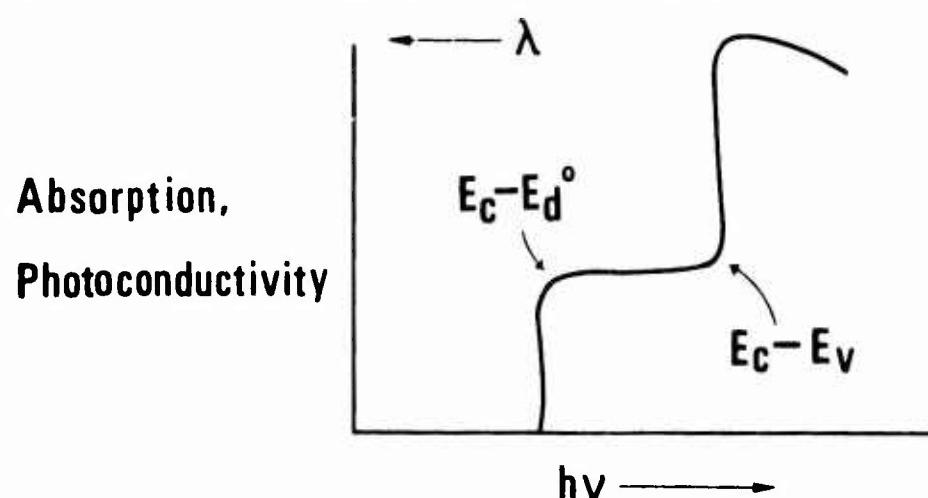
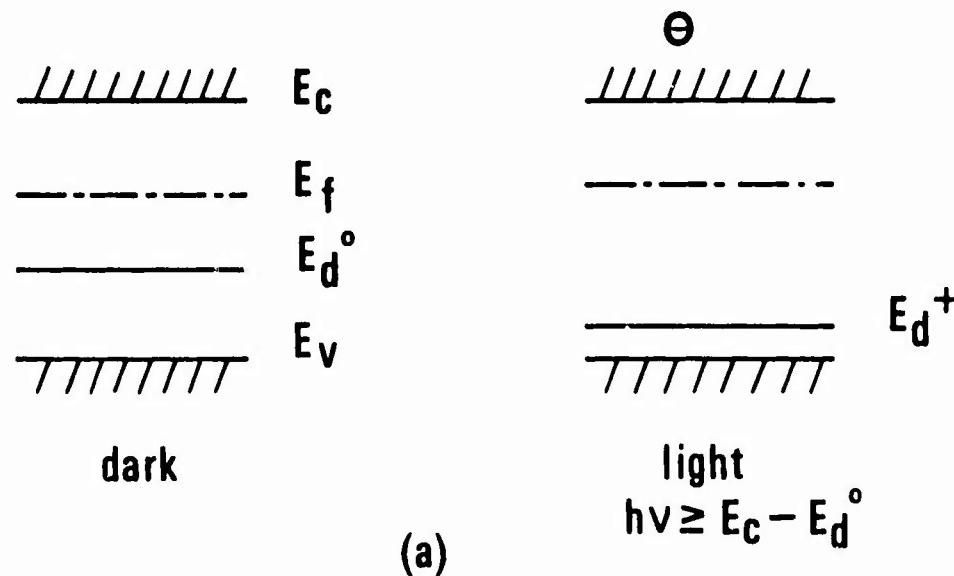
As military requirements for infrared detectors move toward longer wavelength, InSb with its 5.5 micron cutoff becomes an attractive material. Photodiodes are usually fabricated by diffusion of an n- or p-type impurity into p- or n-type material, respectively. Both n-on-p and p-on-n diffused InSb diodes have had limited success; n-type diffusions are very difficult, and p-on-n diodes are adversely affected by the surface properties of InSb (the surface tends to be p-type, resulting in low breakdown voltage and large reverse leakage currents).

One of the earliest radiation effects discovered was the conversion of n-type germanium to p-type after exposure to neutrons in a nuclear reactor (Ref. 1). Subsequently, a similar effect was found for other materials and other irradiation sources. Recently, Foyt and co-workers capitalized on the inverse effect, conversion of p-type InSb to n-type by proton irradiation, to fabricate n-on-p photodiodes (Ref. 7). A dose of 10^{14} protons/cm² at 100 KeV produced diodes with 1 micron junction depth. High yield of good devices is claimed, with the best detectivities being near half the background limited value. Further work on "proton-doped" InSb photodiodes is being performed at NWC by C. Fountain, Code 5525.

SELECTIVE 2.2 μ AND 3.9 μ DETECTORS FROM ELECTRON-IRRADIATED SILICON

Photoconductivity associated with discrete defect levels can be exploited in constructing extrinsic photodetectors. The defect level becomes analogous to Cu or Au impurities in germanium for IR detectors. In the simplest case, shown schematically in Fig. 1(a), a defect acceptor level has trapped an electron and is neutral ($E_d^0 < E_f$). Upon illumination by light with $h\nu \geq E_c - E_d^0$, the trapped electron is ionized into the conduction band, causing an increase in conductivity. The spectral dependence of the absorption and photoconductivity would be identical, as shown in Fig. 1(b).

Most real cases are much more complicated, due mainly to the influence of excited states (Ref. 8). Infrared absorption by defects usually manifests itself as narrow bands occurring at wavelengths



(b)

FIG. 1. (a) A Semiconductor With a Filled Defect Level E_d^0 (left); Light of Energy Greater Than $E_c - E_d^0$ Ionizes the Defect, Producing a Photoelectron in the Conduction Band (right). (b) Spectral Dependence of Optical Absorption and Photoconductivity Resulting From the Defect Level in (a).

greater than the band edge ($E_C - E_V$); these bands correspond to transitions from defect ground states (for example, E_d^0 if $E_f > E_d^0$) to excited states (E_d^o)*. In such a transition the trapped electron is still associated with the defect, so no photoconductivity results. In general, then, there is no correlation between the spectral locations of defect absorption and defect photoconductivity (Ref. 9), which makes it rather difficult to predict the latter.

Photoconductivity associated with two specific defects in electron-irradiated silicon has been exploited by Gross and Mattauch to construct wavelength-selective detectors (Ref. 10). Electrons of 7 MeV were used, with doses in the range $10^{16} - 10^{18}$ per cm^2 . In n-type material at 80°K the spectral response peaks at 2.2μ ; the defect involved is thought to be a vacancy trapped by substitutional phosphorous. In p-type, the divacancy level at $E_V + 0.28 \text{ eV}$ produces a photoconductivity peak at 3.9μ . Two features of these results are not understood: a) the noncorrespondence between photoresponse peaks and known energy levels, as discussed above; b) the existence of maxima in the photoconductivity spectrum (Ref. 11) (according to the simple model of Fig. 1, photoresponse should decrease monotonically with wavelength). Detectivity values in the range $1-4 \times 10^{11} \text{ cm-cps}^{-1}/\text{watt}$ (45° FOV) are reported, indicating fairly good quantum efficiency.

In the geometry used by Gross and Mattauch, the photocarriers had to drift $\sim 3 \text{ mm}$ to be detected; assuming all photocarriers reached the electrodes, the diffusion length L_D must be greater than 3 mm . This implies a lower limit on the 80°K recombination time of $2 \times 10^{-4} \text{ sec}$ for holes, $5 \times 10^{-5} \text{ sec}$ for electrons. These considerations will become important in the next section.

The relative spectral response of irradiated n- and p-type detectors is shown in Fig. 2.

SILICON PHOTODIODE WITH EXTENDED IR CUTOFF

The optimization methods discussed in previous sections were based on discrete defects having essentially atomic dimensions; these were produced by fairly mild irradiations which do not influence the overall lattice perfection. In the case of electron bombardment, there is indirect evidence for the existence of a "disorder threshold energy" above which the defects become more complex (Refs. 12, 13). Two phenomena are observed in silicon when the electron bombardment energy is above this threshold; the absorption edge broadens and shifts to longer wavelength (Ref. 8) [Fig. 3(a)] and the photosensitivity below the edge increases dramatically (Ref. 9) [Fig. 3(b)]. (One-to-one correlation between these two effects has not been established to date; the data in Figs. 3(a) and 3(b) were obtained in different experiments, using widely different total doses.) An additional effect is the reduction

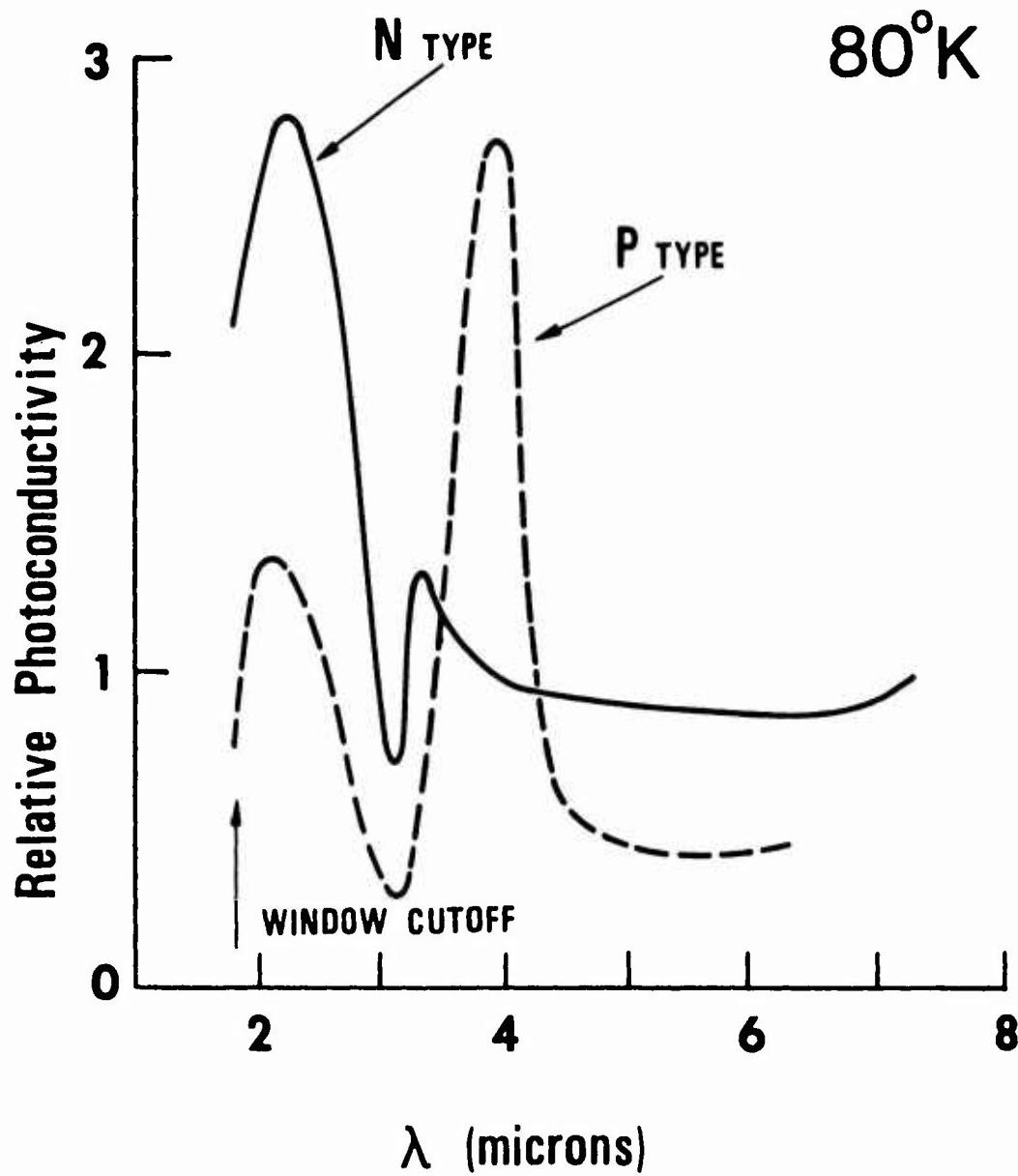


FIG. 2. Spectral Response of Silicon Photoconductive Detectors Fabricated From n- and p-Type Crystals That Were Irradiated With 7 MeV Electrons. The entire response for $\lambda > 1.2 \mu$ is due to radiation-induced defects; different defects are produced in n- and p-type silicon.

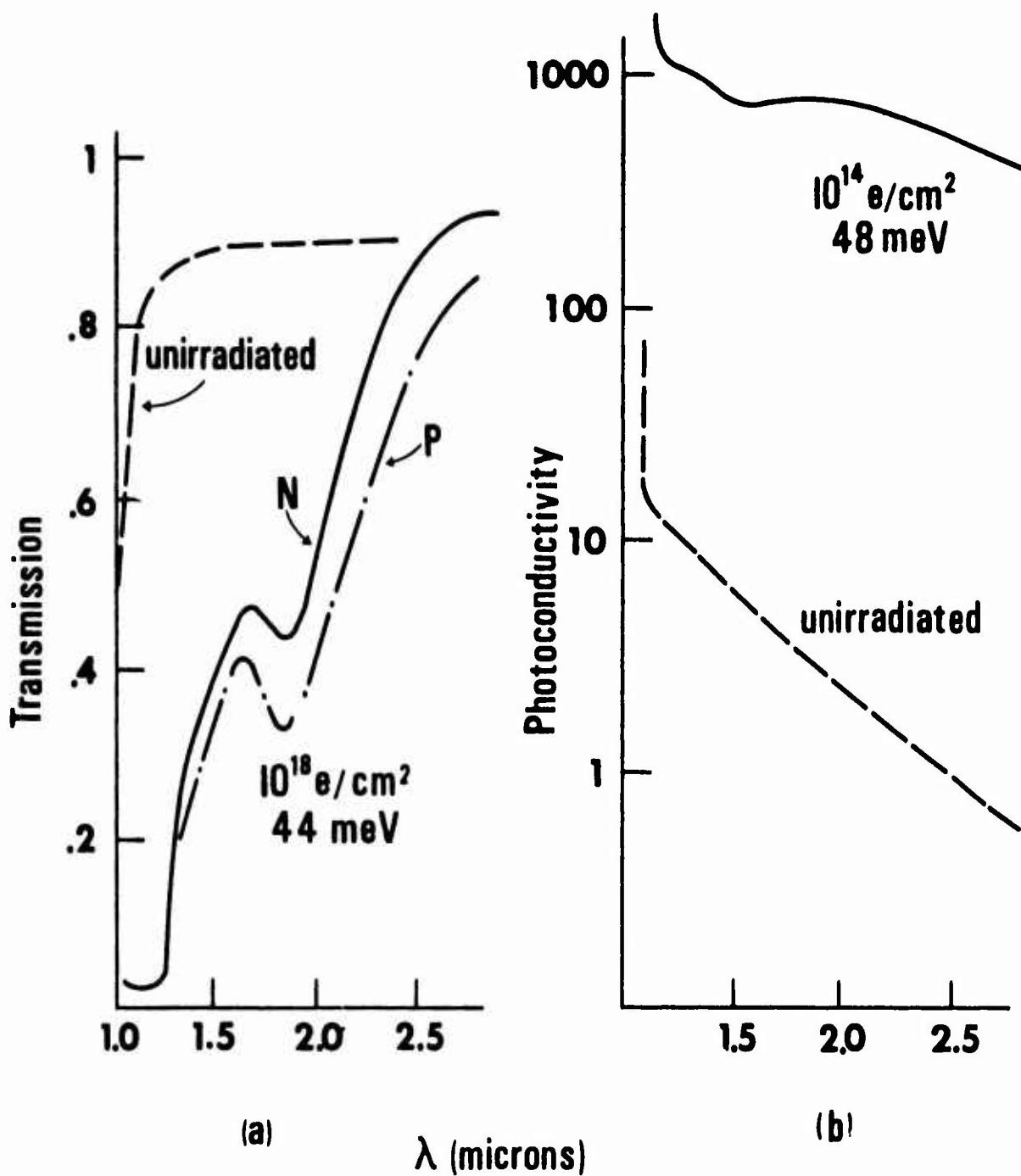


FIG. 3. (a) Alteration of the Absorption Threshold in High-Energy Electron-Irradiated Silicon (after Ref. 8). (b) Near Edge Photoconductivity in High-Energy Electron-Irradiated Silicon (after Ref. 9).

in minority carrier lifetime (Refs. 2, 12); this effect depends critically on initial impurities, as discussed in the first section.

The irradiation effects shown in Fig. 3 can be exploited in two detector applications (keeping in mind the caveats discussed in the preceding section).

Fast 1.06 μ Detection. The design of silicon detectors for the 1.06 μ Nd:YAG laser line requires a compromise between speed and sensitivity. The absorption coefficient at 1.06 μ is normally 25 cm^{-1} , requiring a 10^{-1} cm path to absorb 92% of the light; if 10 nanosecond response is required, the electrode separation cannot exceed 10^{-2} cm . From Fig. 3(a), high energy electron bombardment drastically increases $\alpha(1.06 \mu)$, the absorption coefficient at 1.06 microns, making possible a quantum efficiency of $\geq 90\%$ with a detector 10^{-2} cm thick. In order for this efficiency to be realized in practice, the minority carrier diffusion length L_D must exceed 10^{-2} cm ; otherwise, the photocarriers will combine before being swept to the electrodes.

Near IR (Heat-Seeking) Detectors. From Figs. 3(a) and 3(b), the bombardment-induced absorption and photoconductivity persist into the wavelength range of PbS; detectors made from irradiated silicon could therefore be used in heat-seeking applications. Possible advantages would be room temperature operation, insensitivity to ambients, and reproducibility.

The former application would be the easier of the two to achieve in practice, since less radiation dose would be required [$\alpha(1.06 \mu)$ will increase at a lower dose than $\alpha(2 \mu)$]. Both applications depend on being able to introduce defects which enhance absorption and photoconductivity but do not drastically degrade L_D . This seems impossible at first glance, since L_D is much more sensitive to irradiation than α (see the first section). The situation becomes more hopeful when one considers the individual defects responsible for L_D degradation and enhancement. In the former case, simple point defects (vacancy + oxygen, vacancy + phosphorous, divacancy) play a major role, while more complex clusters control the absorption edge shift (mild irradiations do not affect the edge). The nature of the complex defects is not precisely known, but they seem to be less dependent on impurities than the point defects. In addition, the anneal temperatures are different for simple and complex defects. Therefore, there is some hope of finding a combination of starting material, irradiation dose and energy, and postirradiation heat treatment which will enhance the absorption and photoconductivity without seriously degrading L_D . Now $L_D^2 = D\tau$ where D is the diffusion coefficient and τ is the minority carrier lifetime, so a 10^4 reduction in τ yields only a 10^2 reduction in L_D if D remains constant. From the Einstein relation $D = (kT/e)\mu$, where kT/e is the temperature in eV and μ is the drift mobility; μ is much less sensitive than τ (see first section), so degradation in τ controls L_D . In a pure

perfect crystal $L_D \sim 1$ cm; our fast 1.06 μ detector requires $L_D \sim 2 \times 10^{-2}$ cm for 70% quantum efficiency (assuming 10^{-2} cm thickness). Thus a reduction of 50 in L_D , or ~ 2500 in τ , can be tolerated.

The Schottky barrier photodiode is the ideal structure for testing this approach, because

1. The irradiated specimens will be high resistivity (Refs. 1, 5), thus automatically insuring low leakage.
2. The fabrication process does not depend on crystalline perfection.
3. High temperatures, which would anneal some of the defects, are not required.

The plan of attack in our IED program is as follows:

1. Start with three different impurity levels
 - a. $< 10^{14}/\text{cc}$ oxygen, $< 10^{12}/\text{cc}$ donors
 - b. $\sim 10^{15}/\text{cc}$ oxygen and phosphorous
 - c. $\sim 10^{17}/\text{cc}$ oxygen, $10^{15}/\text{cc}$ phosphorous
2. Irradiate two of each with two different doses of 50 MeV electrons.
3. Anneal one of each at 200°C for 1 hour.
4. Measure α , τ , resistivity.
5. Fabricate Schottky photodiode.
6. Measure spectral response, time constant, leakage current, junction capacitance, noise characteristics.

After evaluating the first group of twelve experimental units, we hopefully will be able to zero in on the optimum combination.

SUMMARY

The effects of nuclear irradiation on semiconductor properties can, in some cases, be exploited in detector design. Gamma ray compensation alleviates the problem of 77°K storage in x-ray spectrometers. Conversion of p-InSb to n-type by proton bombardment allows fabrication of 1 micron deep n-on-p photodiodes with 5.5 μ cutoff. Absorption bands produced in Si by 7 MeV electron bombardment lead to selective IR detectors for 2.2 and 3.9 μ radiation. High energy electron bombardment may yield fast, efficient Si detectors for the 1.06 μ laser line.

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